

# Hydrogen Separation and Purification Using Dense Metallic Membranes

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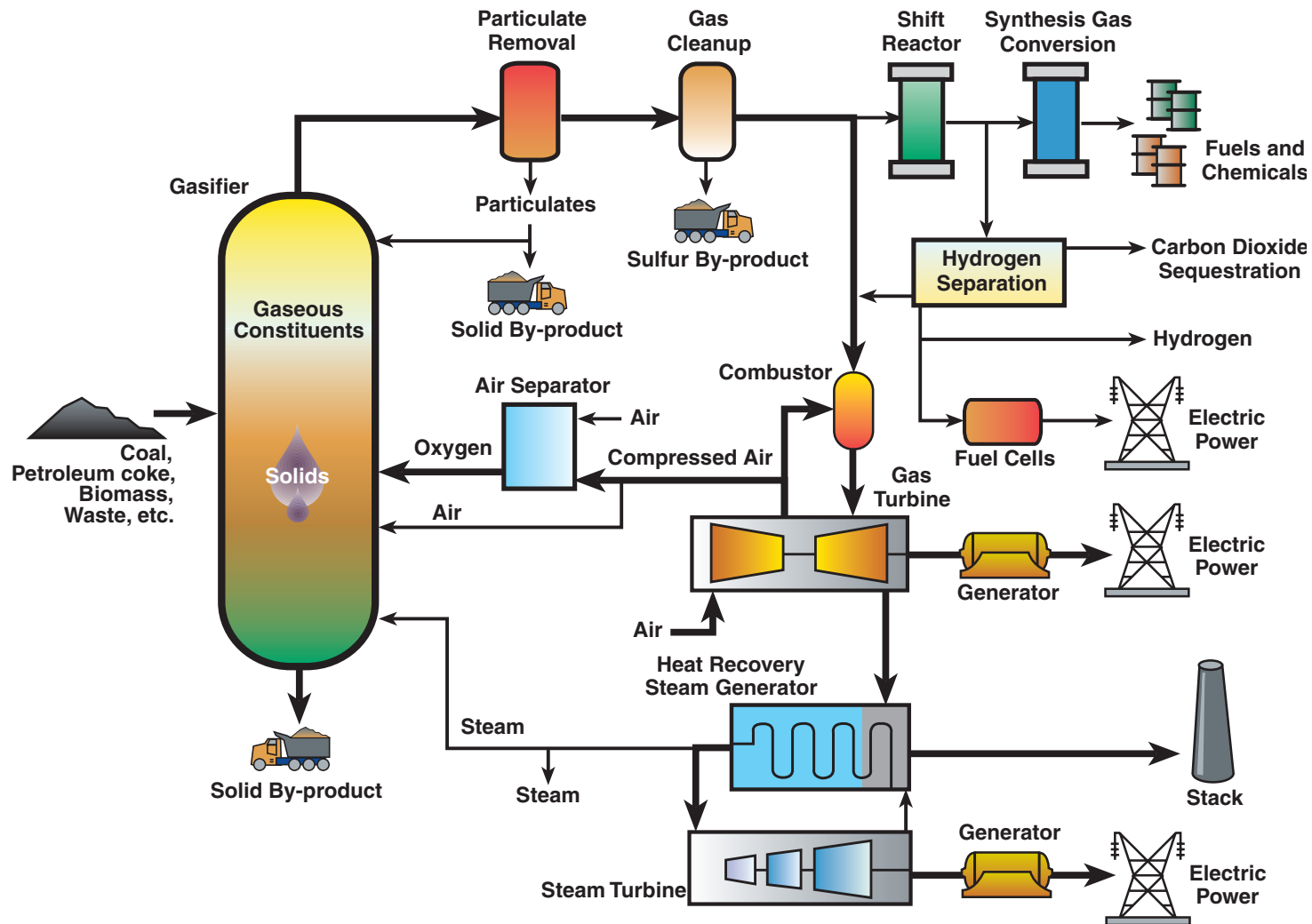
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# **Candidate Commercial Applications**

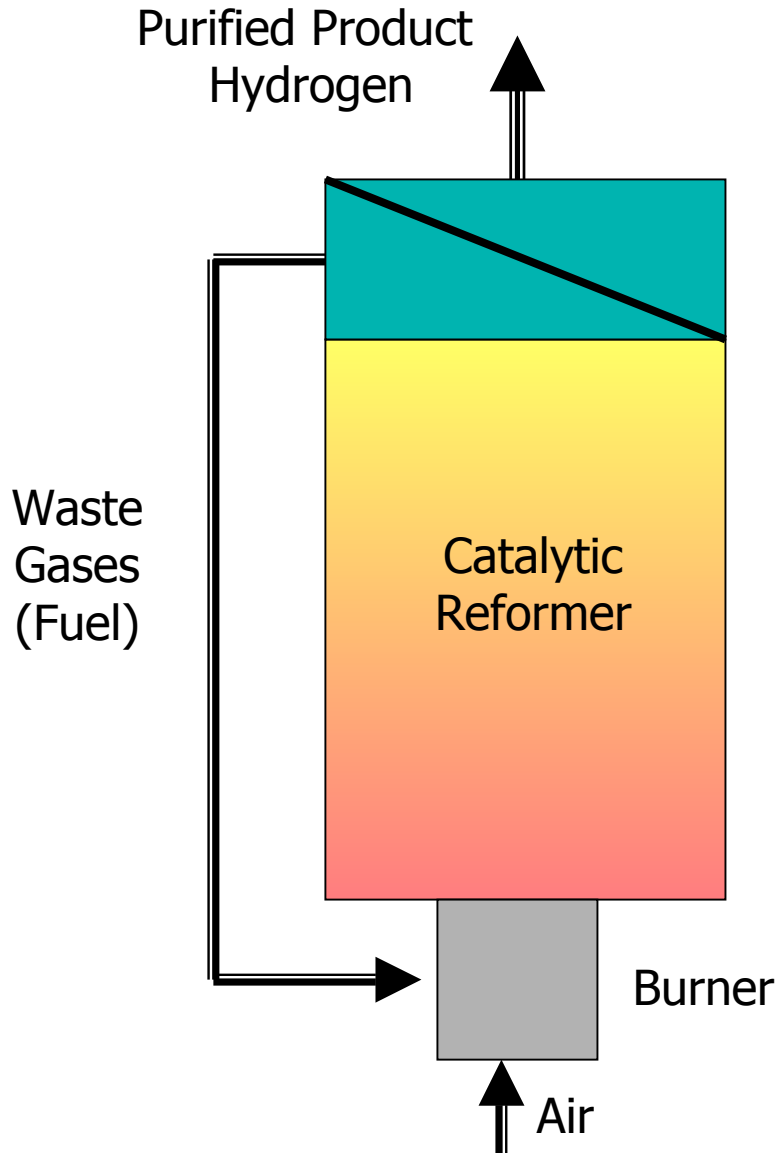
- H<sub>2</sub> production from fossil fuels and renewable fuels
  - H<sub>2</sub> refueling stations
  - Merchant H<sub>2</sub> markets
  - Fuel cell systems
- Hydrogen production from coal gasification (hot syn-gas cleanup)
- Membrane performance has been validated with steam reformers, partial oxidation reactors, autothermal reformers
  - Natural gas
  - LPG
  - Kerosene, diesel, bio-diesel, GTLs
  - Methanol
  - Ethanol

# Hydrogen from Coal Gasification



Courtesy of Dr. Richard Killmeyer, NETL

# Hydrogen from Reformate



- Applicable to any carbon-containing fuel (hydrocarbon or alcohol)
- Steam reforming (externally heated) or ATR (internally heated)
- Membrane should operate in the range of 350°C to 600°C
- Reformate pressure >7 bara

# **High-Purity Hydrogen**

- Solution-diffusion mechanism yields very high-purity permeate hydrogen
  - Selectivity for hydrogen is infinite (assuming no defects in membrane or module)
- Membrane quality can be an issue (defects, composition)
  - Dependent upon fabrication method
  - Also, support structure and composition may influence membrane quality
- Practically, purity is limited by means of module construction (for pin-hole-free membranes)
  - Seals are critical
  - Can add enormous cost to the finished membrane module

# **Non-Metal Membrane Hydrogen Purification Technology**

- PSA (pressure-swing adsorption)
  - Multi-bed process (bulky, valves subject to failure, complex control)
  - Produces high-purity hydrogen (99.9% to 99.9999%)
  - Work-horse of petroleum refining and petrochemical industries
  - World-scale plants will produce 50 million SCFD hydrogen
  - Scales-up well (but does not scale down well)
- Shift reactors coupled with PrOX
  - Yields low-purity hydrogen (typically 20% to 55%)
  - Converts CO to CO<sub>2</sub> by chemical reaction
  - Scales down well but bulky, expensive
  - Control is complex

# Why are Metal Membranes Commercially Attractive?

- Simple to operate
- Reliable (passive operation)
- No moving parts
- High-purity product hydrogen (typically exceeding 99.95%) *independent* of operating state
- Small size
- Flexible (many options for incorporating into an overall system)
- Cost effective solution

# **Candidate Metals for Hydrogen Separation**

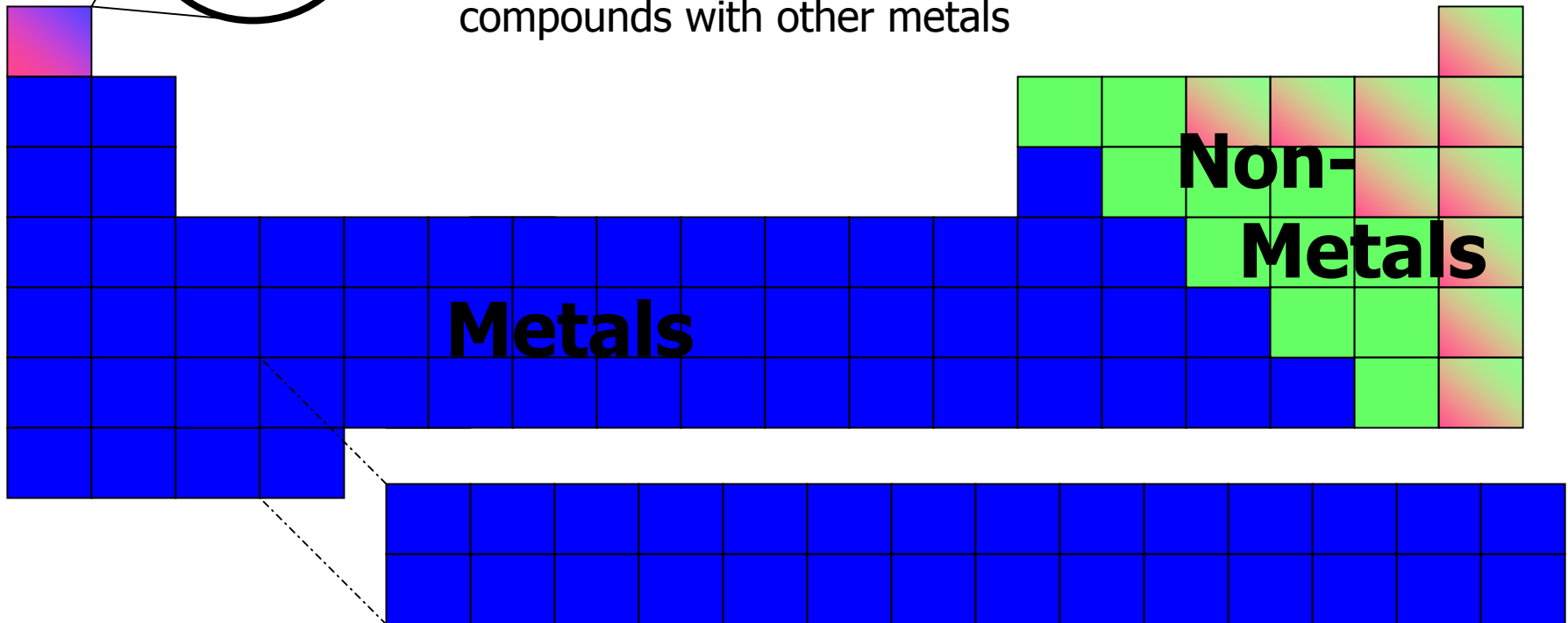
- Pure metals
  - Palladium, vanadium, tantalum, niobium, titanium
- Binary alloys of palladium
  - Pd-40Cu, Pd-23Ag, Pd-7Y, also Pd alloyed with Ni, Au, Ce, Fe
- Complex alloys
  - Pd alloyed with three to five other metals—expensive to fabricate and no clear advantage has been demonstrated
- Amorphous alloys (typically Group IV and Group V metals)
  - Stability has not been demonstrated (thermodynamics favors recrystallization)
  - Kinetic stabilization—what is the effect of dissolved hydrogen and temperature?
- Coated metals
  - Pd over Ta, V, etc.
  - Stability is an issue (intermetallic diffusion)<sup>1</sup>

1. Edlund, D.J., and J.M. McCarthy, The Relationship Between Intermetallic Diffusion and Flux Decline in Composite-Metal Membranes: Implications for Achieving Long Membrane Lifetime, J Membrane Science, 107(1995)147-153

# Hydrogen-Metal Interaction

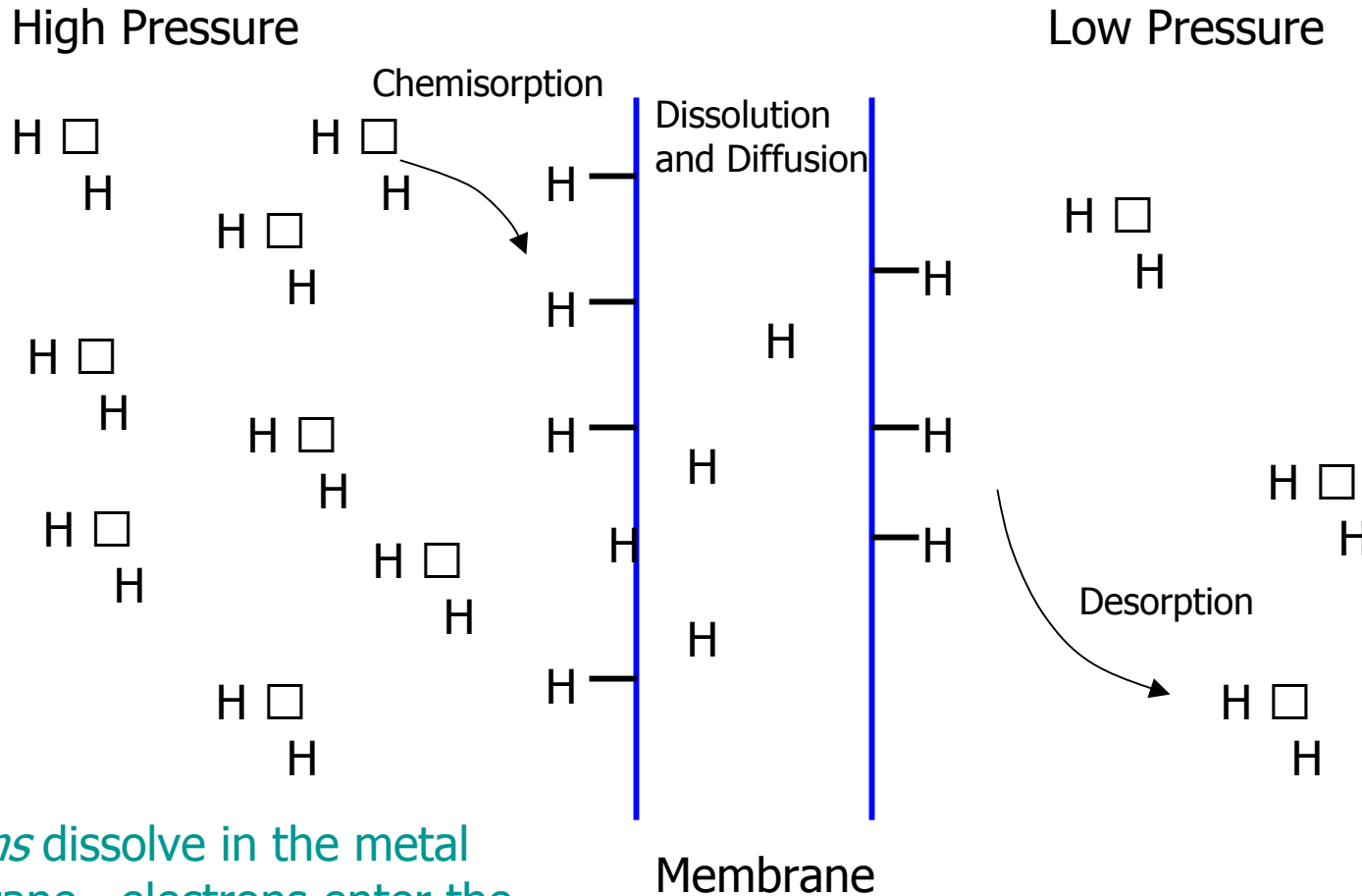
**H**

Hydrogen is a metallic element and forms conventional alloys or intermetallic compounds with other metals



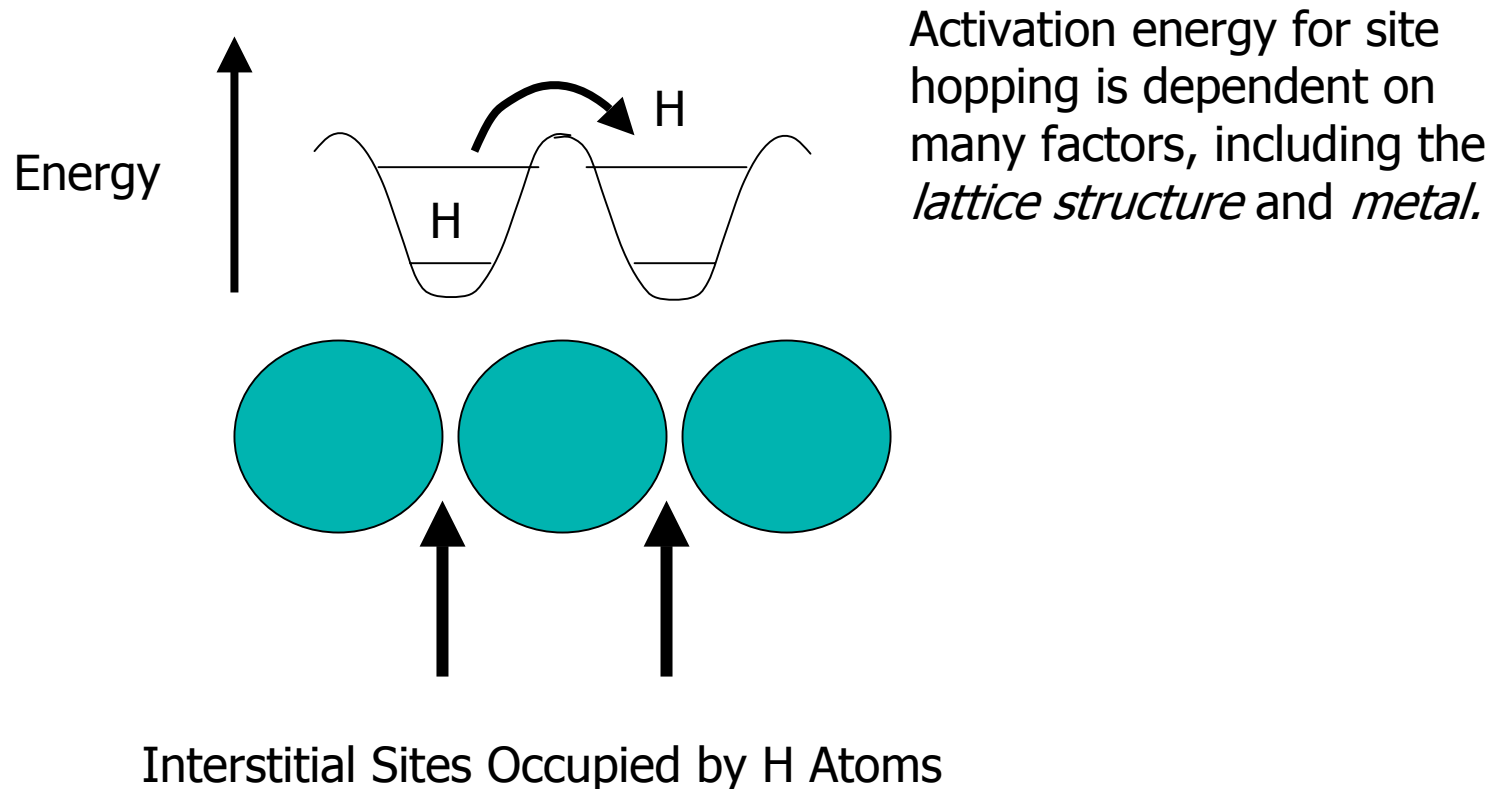
# Hydrogen Permeation in *Metals*

Poisoning occurs when surface reactions are halted



H *atoms* dissolve in the metal membrane—electrons enter the Fermi level of the resulting *alloy*

# Hydrogen Permeation Mechanism



Fukai, Y., and H. Sugimoto, *Diffusion of Hydrogen in Metals*, Advances in Physics, 34(1985)263-326

# Hydrogen-Metal Systems are Dynamic

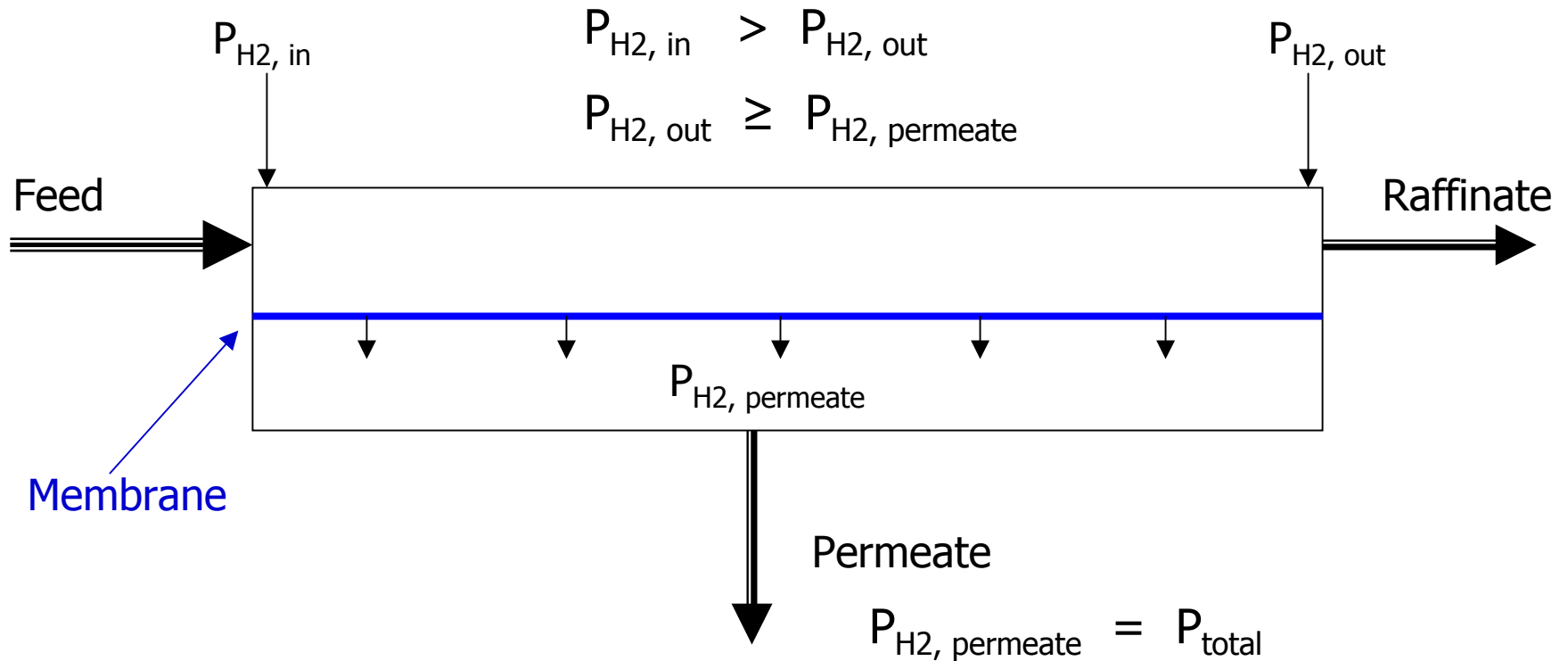
- Hydrogen is an additional *alloying* element
  - Modifies the electronic and physical properties of the host metal
  - Example: a Pd-23Ag membrane in operation is a ternary alloy of Pd, Ag, and H
- The metal membrane will be in contact with other compounds during operation, sometimes with adverse effects
  - Intermetallic diffusion will occur with support metals
  - Carbon contamination can lead to embrittlement (due to carbon dissolution)
  - Example: ethane dehydrogenation over Pd-23Ag at 700°C causes rapid failure of the membrane due to carbon dissolution and embrittlement
  - Poisoning due to non-reversibly surface adsorption of impurities (sulfur, phosphorous, volatile metals)
    - *Not to be confused with reversible adsorption (e.g., CO)*

# Rules of Thumb when selecting an Alloy System

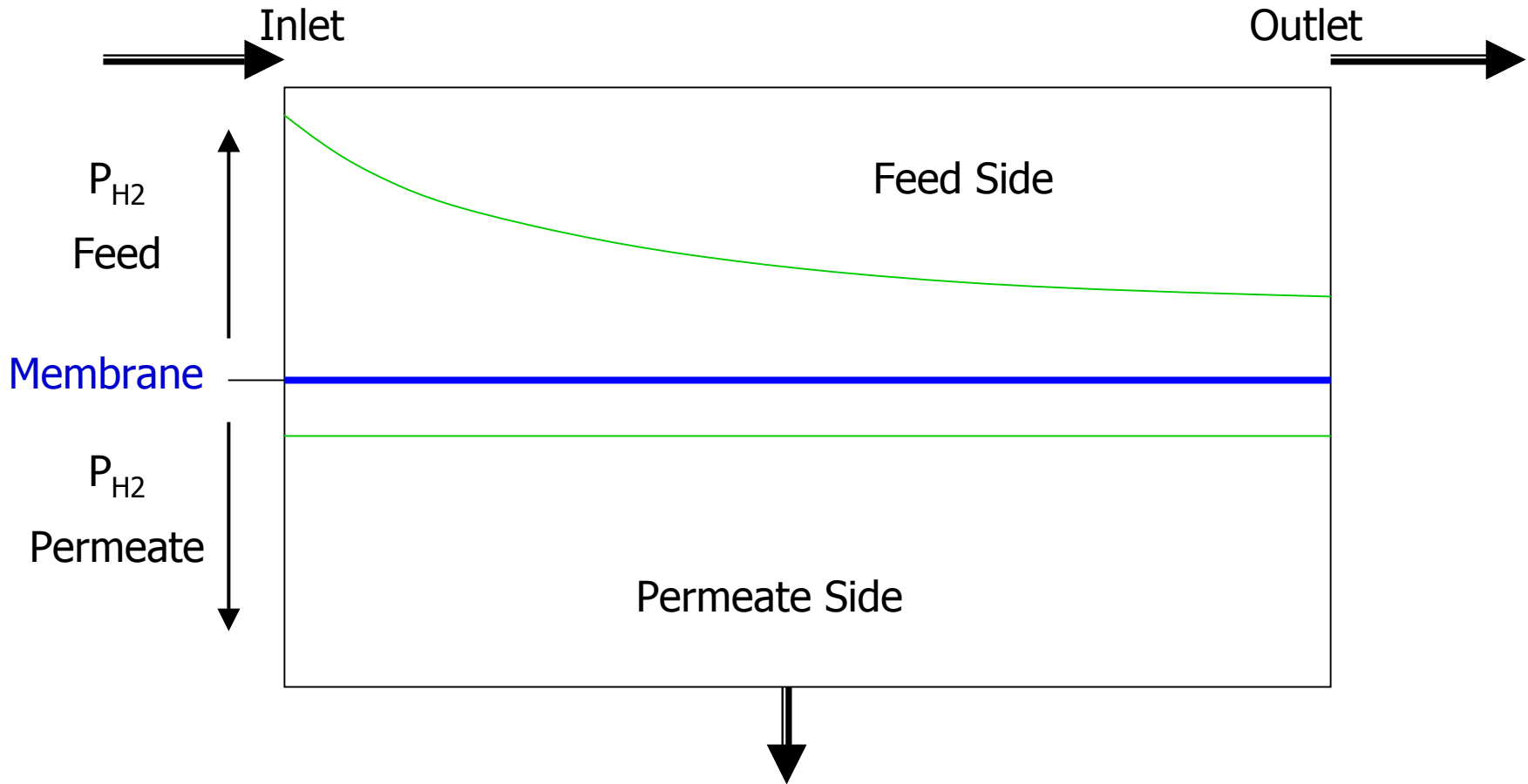
- Avoid alloys that form stable hydrides (intermetallic compounds) under anticipated operating conditions
  - A good metal-hydride storage alloy is not a good candidate for membrane applications
  - Critical temperature
- Open crystal structures are preferred
  - bcc yields higher diffusivity than fcc<sup>1</sup>
- Avoid oxophilic metals (such as the Group III, IV and V metals)
  - Reaction with CO<sub>2</sub>, H<sub>2</sub>O, CO, hydrocarbons will lead to deterioration of the membrane

1. Volkl, J., H.C. Bauer, U. Freudenberg, K. Kokkinidis, G. Lang, K.A. Steinhauser, and G. Alefeld, *Internal Friction and Ultrasonic Attenuation in Solids*, edited by R.R. Hasiguti and N. Mikoshiba, University of Tokyo Press, p.485 (1977)

# $P_{H_2}$ is Important



# Hydrogen Pressure Profile



$$[(P_{H_2,IN})^n - (P_{PERM})^n] - [(P_{H_2,OUT})^n - (P_{PERM})^n]$$

Ln-Mean Driving Force Equals

$$\text{Ln} \left[ \frac{[(P_{H_2,IN})^n - (P_{PERM})^n]}{[(P_{H_2,OUT})^n - (P_{PERM})^n]} \right]$$

Where  $0.5 \leq n \leq 1.0$

# Important Operating Parameters

$$P = D \times S$$

$$P = P_0 e^{-(E_a/RT)}$$

$$J = \text{Permeate Flow Rate}/A$$

$$J \propto (P \times (\Delta P_{H_2})^n)/\ell$$

Where  $0.5 \leq n \leq 1.0$

## Glossary

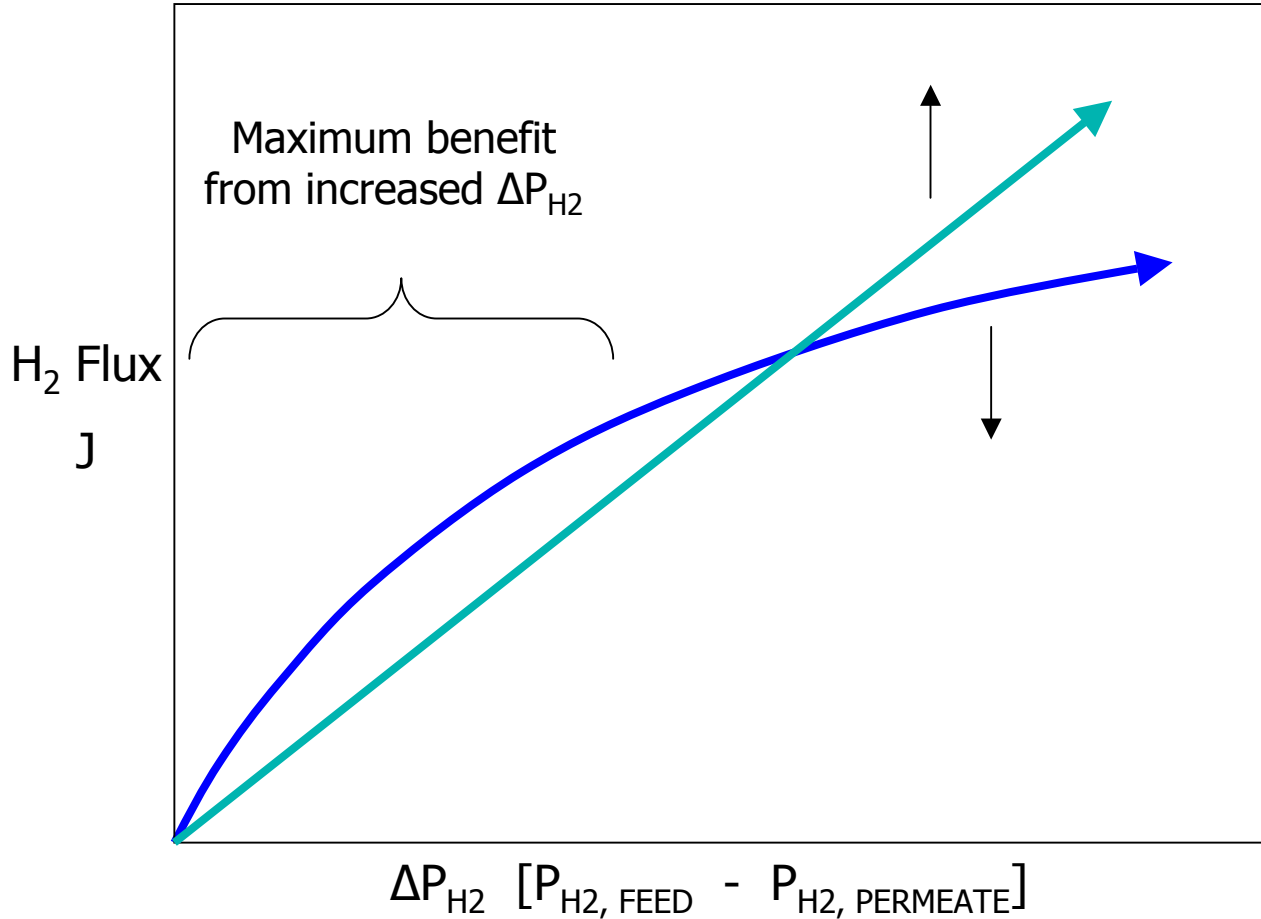
D	Diffusivity of H atoms
S	Solubility of H atoms
P	Permeability of H atoms
$P_0$	Permeability constant
J	Flux of hydrogen
A	Membrane area
$\ell$	Membrane thickness
$\Delta P_{H_2}$	Hydrogen pressure differential
T	Operating temperature

	Increases Flux	Decreases Flux
Increasing D	<input checked="" type="checkbox"/>	
Increasing S	<input checked="" type="checkbox"/>	
Increasing T	<input checked="" type="checkbox"/>	
Increasing A	<input checked="" type="checkbox"/>	
Increasing $\ell$		<input checked="" type="checkbox"/>
Increasing $\Delta P_{H_2}$	<input checked="" type="checkbox"/>	

# Complex Pressure Dependence

$$\Delta P_{H_2} \quad [(P_{H_2, \text{FEED}})^n - (P_{H_2, \text{PERMEATE}})^n]$$

$$0.5 \leq n \leq 1.0$$



## Example Data

113 psia H<sub>2</sub> feed,  $J = 47$

63 psia H<sub>2</sub> feed,  $J = 31$

Permeate at 13 psia,  $J$  is cc/cm<sup>2</sup>·min

$$\sqrt{113} - \sqrt{13} = 7.0$$

$$\sqrt{63} - \sqrt{13} = 4.3$$

$$7.0/4.3 = 1.6$$

$$47/31 = 1.5$$

# **Membrane Module Design**

## *Practical Considerations (Mechanical Engineering)*

- Increasing  $T$  leads to heavier, more expensive membrane module
- Increasing  $\Delta P_{H_2}$  leads to heavier, more expensive membrane module; maybe higher operating costs (compression of feedstream)
- Very thin membranes are not durable, difficult to fabricate (increased cost)
- Increasing membrane area leads to higher costs

# **DoE's Stated Targets and Status**

Characteristics	Units	2003 Status	DoE Target
Flux Rate	Std. cc/cm <sup>2</sup> •min	30	100
	scfh/ft <sup>2</sup>	60	200
Cost	\$/ft <sup>2</sup>	150-200	<100
Durability	Hours	<1,000	100,000
Operating Temperature	°C	300-600	300-600
Parasitic Power	kWh/1,000 scfh	3.2	2.8

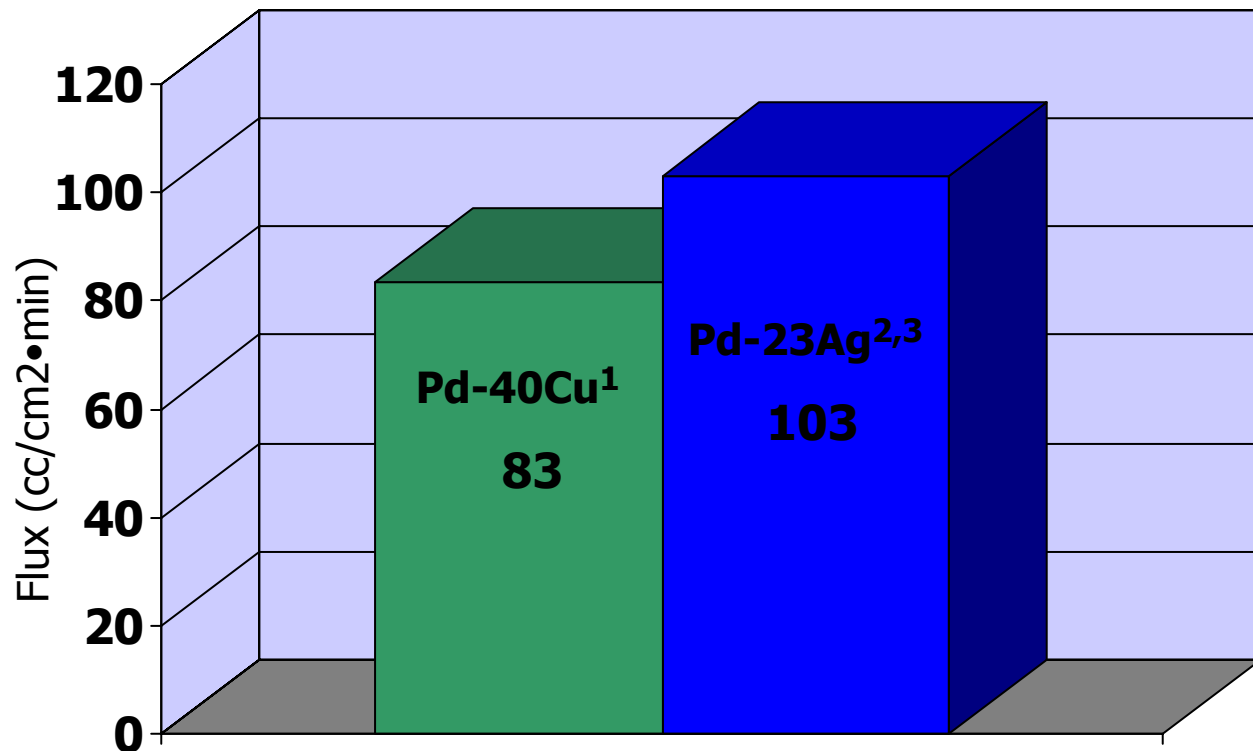
# **Binary Alloy Comparison**

Characteristics	Units	Pd-40Cu	Pd-23Ag
Pd content	Weight %	60	77
Standard flux (25 $\mu\text{m}$ thick) <sup>1</sup>	Std. cc H <sub>2</sub> /cm <sup>2</sup> •min	50 <sup>2</sup>	79 <sup>3,4</sup>
Normalized flux <sup>5</sup>	Std. cc H <sub>2</sub> /cm <sup>2</sup> •min	83	102
Embrittled by hydrogen	N/A	No	No
Poisoned by sulfur	N/A	No	Yes

1. Flux rate is measured at 115 psia pure hydrogen feed pressure, 15 psia permeate pressure, 400 °C , and using a 25-micron-thick membrane.
2. Experimentally measured by IdaTech.
3. Ali, J.K., J. Newson, and D.W.T. Rippin, "Deactivation and Regeneration of Pd-Ag Membranes for Dehydrogenation Reactions" J. Membrane Sci., 89(1994)171-184.
4. Ackerman, F.J., and G.J. Koshinas, "Permeation of Hydrogen and Deuterium Through Palladium-Silver Alloys" J. Chemical and Eng. Data, 17(1972)51-55.
5. Standard flux divided by weight-percentage of palladium.

# Palladium-Normalized Flux Analysis

- Cost increases with Pd content (assuming easy to fabricate alloys)
- Normalize  $H_2$  flux to Pd content
- Result provides meaningful basis for comparisons
- NOTE: Not all alloys are stable

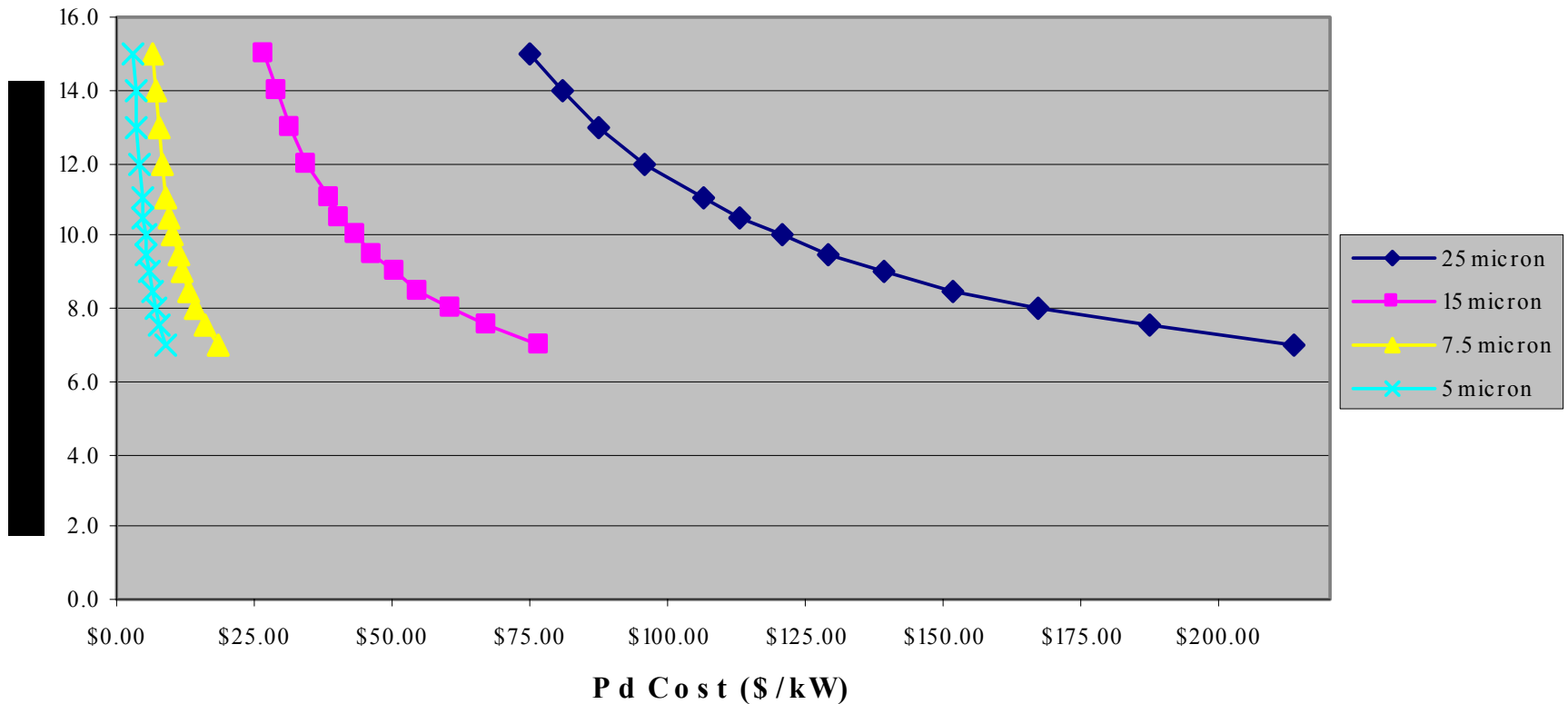


1. Measured by IdaTech

2. J.K. Ali, E.J. Newson, D.W.T. Rippin "Deactivation and Regeneration of Pd-Ag Membranes for Dehydrogenation Reactions" J. Membrane Sci. 89(1994)171-184

3. F.J. Ackerman, G.J. Koskinas "Permeation of Hydrogen and Deuterium Through Palladium-Silver Alloys" J. Chemical and Eng. Data 17(1972)51-55

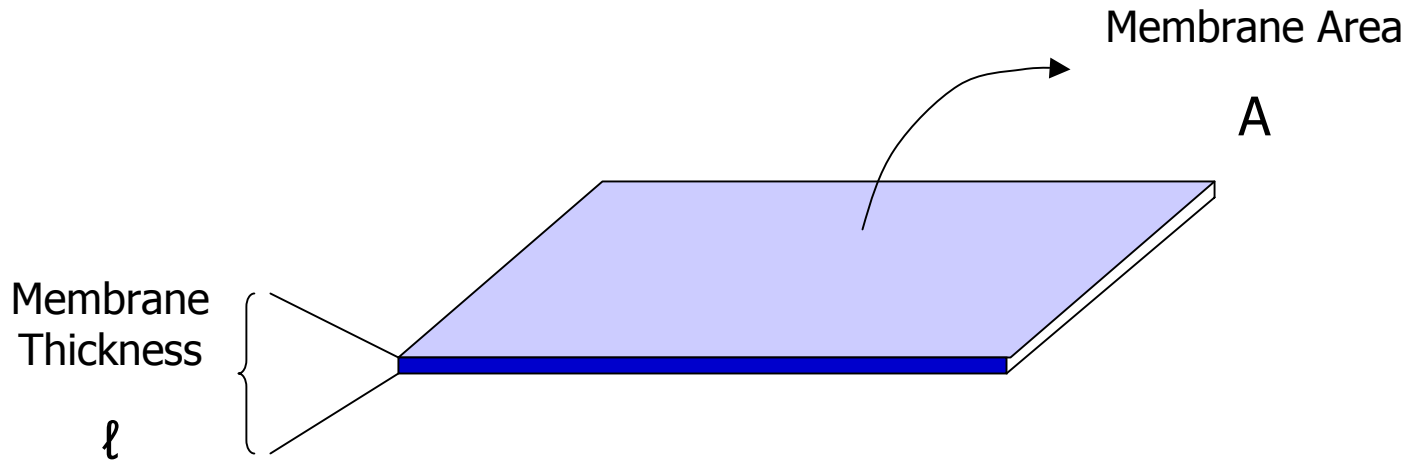
# Palladium Membrane Cost Analysis



Basis: 53% H<sub>2</sub> in feed, 1.25 bara permeate, \$350/oz Pd, 70% H<sub>2</sub> recovery

NOTE: \$/kW is equivalent to \$/12 sLm H<sub>2</sub>

# Why is Membrane Thickness So Important?



Assume membrane thickness is reduced by 3x (e.g., 25  $\mu\text{m}$  to 8  $\mu\text{m}$ )

For  $\ell = 25 \mu\text{m}$ ,  $\text{H}_2$  flux =  $J$

For  $\ell = 8 \mu\text{m}$ ,  $\text{H}_2$  flux =  $J/0.33$  or  $3J$

Then, to maintain constant  $\text{H}_2$  flow rate, only need 1/3 of the original membrane area  $A$

So, Pd content is reduced to  $0.33 \times 0.33$  or 0.11 of original amount. . .  
*This is a **9-fold reduction** in the Pd requirement!!!*

# Various Fabrication Methods

Method	Pros	Cons
Rolling	<p>Common, high-volume fabrication method.</p> <p>Excellent quality can be obtained.</p> <p>Thickness <math>\geq 2</math> microns.</p>	<p>Not easily adapted to small samples.</p> <p>Quality is controlled by metallurgy of the billet.</p> <p>Long process lead time.</p>
Vapor Deposition	<p>Can yield <math>&lt; 2</math> micron films.</p> <p>Easily adapted to small samples.</p> <p>Quick turn around.</p>	<p>Generally poor quality (difficult to avoid pin holes, contamination).</p> <p>Generally applied to a support, may limit flexibility.</p>
Solution Plating		

# **Two Physical Designs Classes**

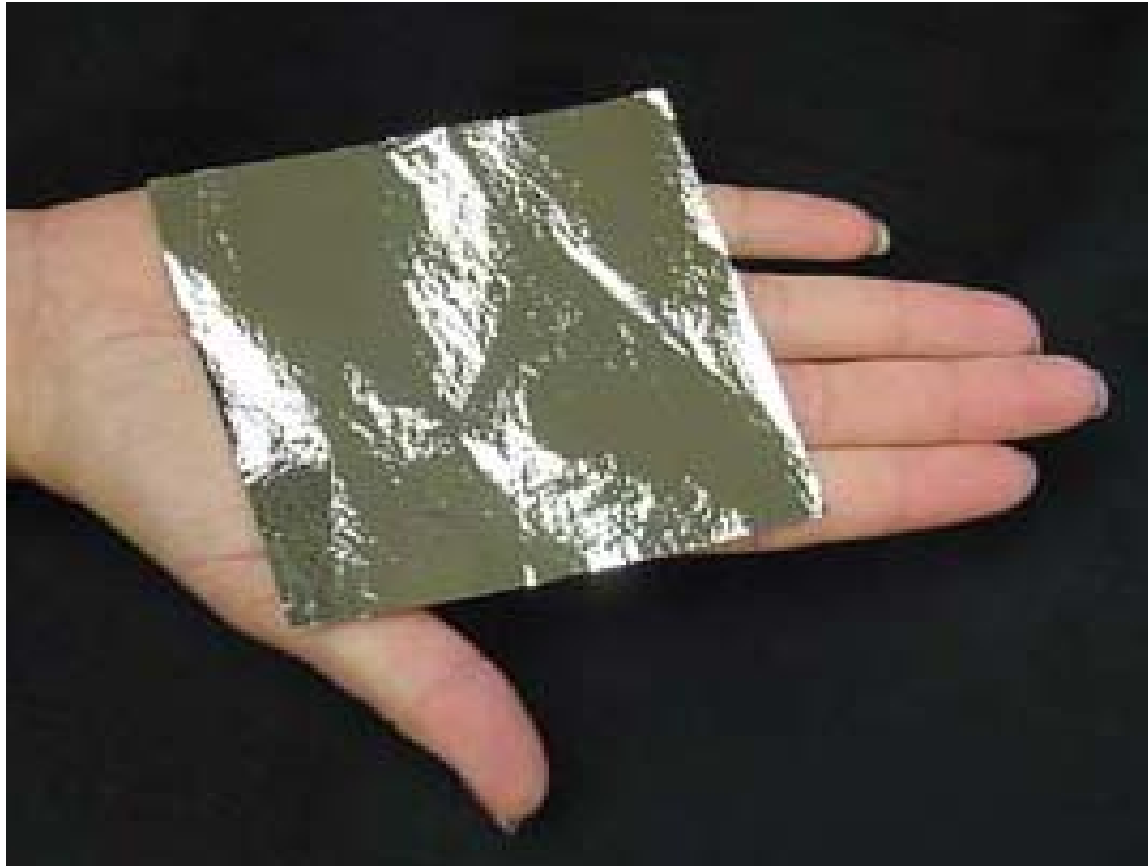
## ■ Tubular

- Typically small-diameter tube, maybe 100-150  $\mu\text{m}$  O.D. with a 25-50  $\mu\text{m}$  wall thickness
- Welded or brazed to a header
- Often several meters in length
- Inside feed » best combination of strength and low mass transfer resistance
- Low packing density (membrane area per unit of volume)

## ■ Planar

- Typically thin foils » mechanical support is required to have any degree of mechanical strength
- Seals can be achieved by gaskets, brazing, or welding
- High packing density

# A Binary Palladium Alloy Foil

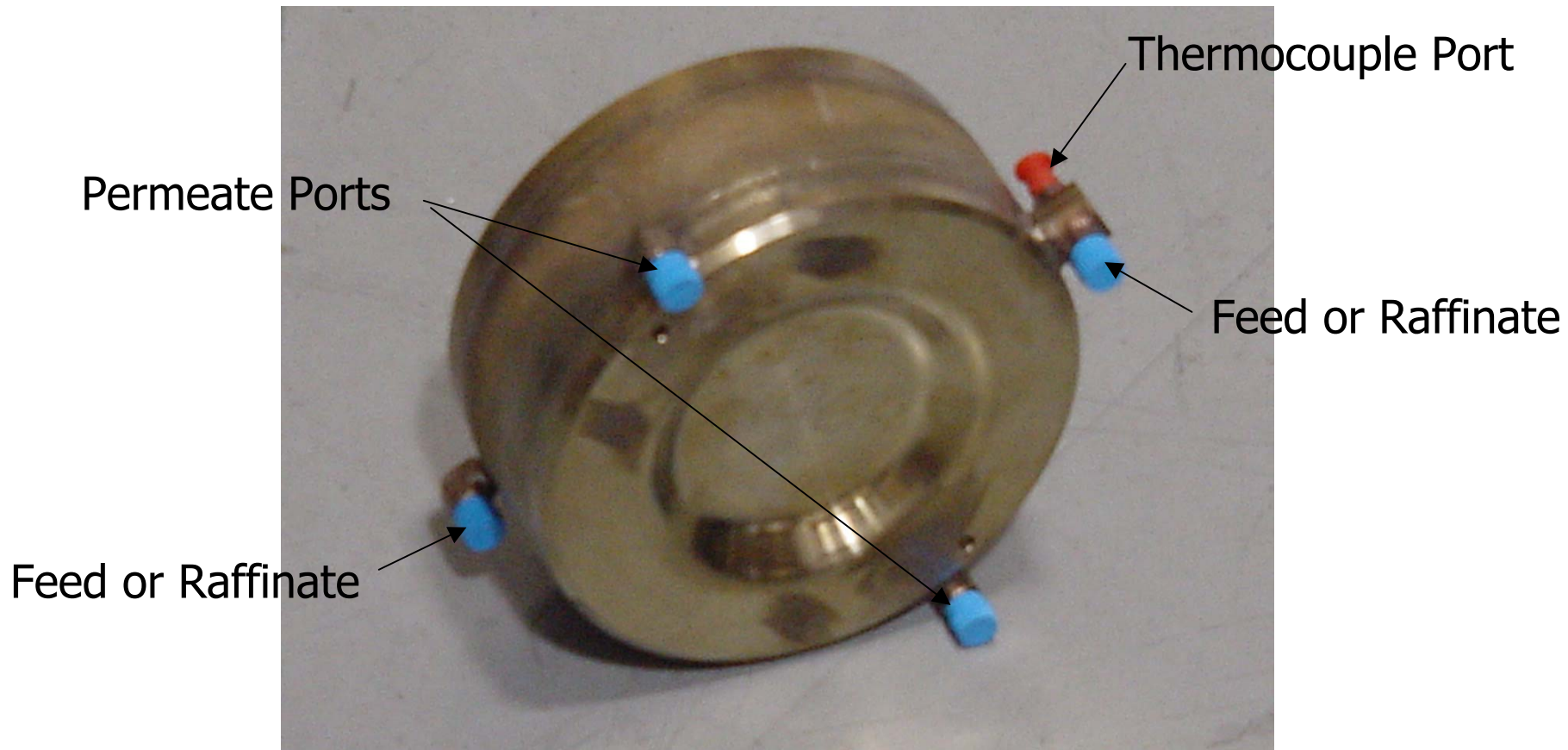


- 5 microns thick, pin-hole free
- Pd-40Cu alloy: this alloy exhibits remarkable tolerance to sulfur<sup>1,2</sup>
- Fabricated by conventional rolling
- Approximately 10 cm x 10 cm, fabricated as continuous roll

- Edlund, D., *A Membrane Reactor for H<sub>2</sub>S Decomposition*, Department of Energy Contract #DE-FG03-92ER81419, paper presented at the Advanced Coal-Fired Power Systems '96 Review Meeting, Morgantown, WV (July 16-18, 1996)
- Morreale, B.D., M.V. Ciocco, B.H. Howard, R.P. Killmeyer, A.V. Cugini, and R.M. Enick, *Effect of Hydrogen-Sulfide on the Hydrogen Permeance of Palladium-Copper Alloys at Elevated Temperatures*, J Membrane Science, 241(2004)219-224 and references therein

# Example of a Planar Membrane Purifier

*Lifetime >35,000 hours has been demonstrated*



# **Technological Limitations**

- Requires narrow range of operating temperature with most feed streams (about 350°C-550°C)
  - Low temperatures and high temperatures are problematic
- Relatively large  $\Delta P$  is required
  - Remember, it is hydrogen partial pressure that governs performance
- Feed stream contaminants may be a concern
  - “Poisons” such as sulfur compounds, heavy metals, etc. will also poison catalysts in upstream unit operations
  - But coal-derived syngas may have particulates and sulfur compounds (prior to shift reactors)

# **Current Activities in Metal Membrane Technology**

- Commercial/Pre-commercial Products
  - Electrolyzers (purification of product hydrogen: Proton Energy Systems, Parker, Matheson)
  - Compact fuel processors for fuel-cell systems (purification of hydrogen from reformat: IdaTech, Genesis Fueltech, MesoFuel, InnovaTek)
  - Stand-alone hydrogen generators (purification of hydrogen from reformat: IdaTech)
- Research and Development
  - USA: NETL, Colorado School of Mines, Tufts University, INEEL, SwRI, Hy9, Power & Energy, Worcester Polytechnic Institute
  - Japan: Fukuda Metals, Tokyo Inst. Of Techn., Nikko Materials, Mistubishi Materials, Nissan, Toyota, Tokyo Gas
  - Europe: University of Twente, W.C. Heraeus

# Challenges and Opportunities

## *Cost Reduction is the Name of the Game*

- **Capital Cost:** Reduce membrane thickness to  $\leq 12$  microns
  - Achieve acceptable manufacturing yields of the membrane
  - Develop robust and affordable membrane module designs
- **Operating Cost:** Demonstrate durability
  - Long-term testing: is crystal structure stable? Creep? Other metallurgical changes?
  - Membrane-support interactions?
  - Discovery new alloys that broaden range of operating temperature (lower and higher)

# **Questions & Answers**